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        This project was concerned with the development of theoretical methods for describing atomic and molecular processes that are important in high performance combustion applications, in plasmas, in the upper atmosphere, and in Low Earth Orbit. The methods involved a combination of electronic structure and molecular dynamics approaches, with emphasis on methods for describing the motions of nuclei where forces are derived directly from electronic structure theory. For gas-phase processes, these so-called "direct dynamics" methods used density functional theory forces, while for gas-surface processes, mixed quantum/classical methods were developed.

        A particular focus of the research was on electron-molecule collisions that lead to fragmentation into neutral radical species. Here a theory of electron-impact-excitation-dissociation was developed, and used to study the electron-induced fragmentation of methane as well as its VUV photodissociation. The direct dynamics technology was also used to study a number of bimolecular reactions at hyperthermal energies. The studies of the reactions of atoms and ions with liquids focused on O and F atoms reacting with squalane or ionic liquids. Other studies considered the reaction of atomic oxygen with graphite and graphite oxide surfaces. In all of these studies detailed comparisons with experiment were made, providing a key link between what is observed and the underlying reaction mechanisms.

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Final Performance Report
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Executive Summary

This project was concerned with the development of theoretical methods for describing atomic and molecular processes that are important in high performance combustion applications and in plasmas. Some of these methods also have applications to ion chemistry in the upper atmosphere, and to chemistry that is important to Low Earth Orbit (LEO) spacecraft. Specific applications we considered included electron, atom and ion collisions with small molecules, and atomic or ion collisions that occur at gas/liquid and gas/solid interfaces.

The theory methods we have developed involved a combination of electronic structure and molecular dynamics approaches, with emphasis on methods for describing the motions of nuclei where forces are derived directly from electronic structure theory, either for a single Born-Oppenheimer potential energy surface, or for nonadiabatic dynamics. For gas-phase processes, these so-called "direct dynamics" methods used density functional theory forces while for gas-surface processes, approximate electronic structure calculations (semiempirical methods) were used to describe the part of the system where bond-breaking/formation takes place while empirical potentials were used for the remainder, leading to a QM/MM direct dynamics method.

A particular focus of the research was on electron-molecule collisions that lead to fragmentation into neutral radical species. Here we developed a theory in which integral cross sections for electron-impact-excitation are calculated with a scaled Plane Wave Born approximation, and the dissociation branching was described using trajectory surface-hopping (TSH) using CASSCF methods to provide forces and nonadiabatic couplings. Preliminary results based on this approach have been generated for the electron impact dissociation of methane. A more detailed study using the TSH method was performed for the VUV photodissociation of methane, where excellent agreement with measured branching and fragment energy distributions was found. The direct dynamics technology was also used to study a number of bimolecular reactions, including the reaction of hyperthermal atomic oxygen with HCl, H_2O, ethane and ethylene, the reaction of O_2 with CO_2, the reaction of $S(^1D)$ with HD, and the reaction of O^+ with HCN.

Our studies of the reactions of atoms and ions with liquids focused on developing QM/MM methods to do direct dynamics calculations based on semiempirical methods for the QM atoms and empirical force fields for MM atoms with the partitioning between QM and MM atoms allowed to vary with time. Applications included studies of O and F atoms reacting with squalane, and the reaction of O with an ionic liquid. We also studied the reaction of atomic oxygen with graphite and graphite oxide surfaces. In all of these studies we made detailed comparisons with experiment, providing a key link between what is observed (typically gaseous species that come off the surfaces) and the underlying reaction mechanisms.

Personel associated with the project were: Wenfang Hu (grad student who finished her Ph. D. in 2007), Jon Camden (postdoc, now a faculty member at Tennessee), Dongwook Kim (postdoc, now at Georgia Tech), Jeff Paci (postdoc), Maricris Lodriguito (postdoc) and Scott Yockel (postdoc). Here is a list of the papers that resulted from this project.

(1) Direct dynamic simulations of $O(^3P)$ + HCl at hyperthermal energies, Jon P. Camden and George C. Schatz, J. Phys. Chem. A 110, 13681-13685 (2006).

(2) Theoretical investigation of hyperthermal reactions at the gas-liquid interface: $O(^3P)$ and squalane, Dongwook Kim and George C. Schatz, J. Phys. Chem. A 111, 5019-31 (2007).

(3) Using theory and computation to model nanoscale properties, G. C. Schatz, PNAS 104, 6885-92 (2007).

(4) Significant nonadiabatic effects in the $S(^1D)$ + HD reaction, Tian-Shu Chu, Ke-Li Han and George C. Schatz, J. Phys. Chem. A 111, 8286-90 (2007).

(5) Crossed-Beams and Theoretical Studies of the $O(^3P)$ + $H_2O \rightarrow HO_2$ + H Reaction Excitation Function, A. L. Brunsvold, Jianming Zhang, Hari P. Upadhyaya, Timothy K. Minton, Jon P. Camden, Jeffrey T. Paci and George C. Schatz, J. Phys. Chem. A, 111,10907-13 (2007).

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I. Introduction

The development of advanced engines for high performance aircraft and for space vehicles continues to provide important basic science challenges where fundamental discoveries can have important impact. A recent example of this has concerned the development of electrospray thrusters for spacecraft engines based on ionic liquids.[1] This technology has gone from basic research to practical implementation over the last 10 years as a result of advances in ionic liquid and electrospray technology. Another example arises in plasma-assisted combustion where there have been important advances in the last 10 years leading to practical devices.[2,3] However important challenges (and opportunities) exist for other technologies. The development of improved fuels for supersonic and hypersonic jet aircraft remains an important goal, but it is a complex goal as the fuel must not only have high energy content, and useful ignition characteristics, it must also have significant thermal stability and hydrodynamic properties due to its use as the cooling fluid in high performance aircraft.[4] Plasma assisted combustion depends on the efficient degradation of fuel molecules into radical species that promote chain reaction mechanisms that result in combustion,[5] but radicals can also produce soot[6] that can clog engines. Currently the degradation mechanisms that lead to radical formation

are poorly understood even for well-known fuels.[6-8] With new classes of fuels, it is important to have the means to model neutral radical yields relatively quickly so that the virtues and weakness of these fuels can be efficiently assessed. In addition, chemical reactions in plasmas can considerably influence turbulent combustive flow,[9] but because of the high energies involved, the important reactions are often unknown or uncharacterized. Another important challenge arises when vehicle components (or engine components) are exposed to harsh environments (plasmas, hyperthermal atoms, very high temperatures) such as arise in hypersonic flight, rocket engines, Low Earth Orbit (LEO), or reentry problems.[10-14]

Computational modeling often provides a useful approach to study these complex problems, particularly if coupled with experiments which provide molecular level information for calibration.   This report describes a program of research aimed at developing theoretical/computational methods designed to describe dynamical processes of current interest where bond formation and breaking are involved, and where describing the dynamics at the atomic/molecular level is essential. The processes of interest included some of the examples given above, particularly the fragmentation of fuel molecules by electron impact and reactions involving ionic liquids (here considered as a fuel rather than for electrical propulsion). We also examined chemical reactions important in LEO or in upper atmospheric plasma chemistry that involve hyperthermal atoms or ions, and the degradation of carbon-based surfaces by energetic atoms or ions.

The computational methods were based on a combination of electronic structure and trajectory-based collision dynamics approaches, with emphasis on methods for describing the motions of nuclei in which forces are derived directly from electronic structure theory, either for processes which can be described with a single Born-Oppenheimer potential energy surface, or for nonadiabatic (multiple surface) dynamics. For gas-phase Born-Oppenheimer collision processes, this class of methods becomes what are often called "direct dynamics" methods, wherein the forces are typically derived from density functional theory calculations. Higher quality correlated calculations based on coupled cluster or multireference electronic structure methods are possible, but because a typical trajectory requires thousands of force evaluations, there is a premium on finding the most efficient methods that produce an acceptable level of accuracy. For gas-surface processes where many thousands of atoms are involved, it is necessary to use even simpler electronic structure methods such as semiempirical or tight-binding methods, and even with this it is usually necessary to combine these calculations for the part of the system where bond-breaking/formation takes place with empirical potentials for the rest, leading to a QM/MM direct dynamics method.

In the following sections we describe the methods and applications in a number of directions: (1) hyperthermal bimolecular collisions in the gas phase, (2) electron-induced fragmentation and photodissociation of methane, and (3) gas-surface reactions.

II.1 Hyperthermal collisions involving small molecules and ions

Reactive and inelastic collisions involving small molecules provide an excellent example for the development and testing of direct dynamics methods. In addition, the study of hyperthermal collision processes (involving few eV energies) is a relatively new field of study which has been of interest recently as a result of new crossed beams experiments which are able to produce hyperthermal atoms and molecules and probe the subsequent dynamics (thus mimicking LEO processes which were not previously accessible to terrestrial experiments). In our work in this area, we have done both theory development and applications, with the

development work concerned with taking advantage of improved electronic structure models, and accelerated convergence, together with new dynamics codes for describing a diverse set of properties and experimental conditions which are important to our applications.

A new development in the last three years has involved improved density functional theory methods for describing reactive potential energy surfaces. Density functional theory methods provide a practical approach for doing direct dynamics calculations which we have used in several studies in this project, typically using the B3LYP functional.[15-17] However a limitation in this work has been with the quality of the surfaces for reactions where barrier crossing is important. Thus B3LYP can have barriers that are off (typically low) by 3-10 kcal/mol or more, and as a result we have always needed to calibrate our B3LYP calculations using coupled-cluster (CCSD(T)) methods. In addition[15,16] we have used direct dynamics based on correlated wavefunction methods such as MP2 to provide guidance. However a new generation of hybrid density functional methods has appeared which significantly improves on B3LYP. In one study of O + HCl[15] we demonstrated that the BMK functional leads to noticeably better results (threshold energies, peak cross sections, angular distributions) compared to B3LYP with no additional computational effort for direct dynamics studies.

In a collaboration involving Jan Martin (Weizmann)[18] we developed a new class of *double* hybrid functionals that is significantly better than the standard hybrid functionals, including both B3LYP and BMK, with close to 1 kcal/mol accuracy for barriers. The double hybrid functionals have not yet been developed for direct dynamics calculations, but this appears to be an extremely promising direction of research.

Our applications work has emphasized hyperthermal oxygen atom collisions with HCl,[15,17] H_2O[16], and ethane.[19] These calculations predicted new reaction channels (particularly for hydrogen atom elimination) that have subsequently been verified by experiment.[16,17,19] We have also studied the reaction of atomic ions with small molecules, particularly O^+ with methane,[20,21] where we found that the complex branching patterns observed at several eV energies could be understood in terms of families of reaction mechanisms based on calculations with the PM3 semiempirical Hamiltonian. An analogous study of O^+ + HCN,[22] which provides a successful explanation for the observed branching[23] between several possible product channels and which includes useful predictions about products that have yet to be investigated, has also been completed. In addition to this work, we have collaborated with Mitchio Okumura and Tim Minton in a study of the reaction of molecular oxygen (O_2) with CO_2,[24] showing that although the barrier to isotope exchange has the extremely high value of 150 kcal/mol, this process is detectable at 10 eV collision energies.

A big challenge with direct dynamics calculations is the description of nonadiabatic processes where the electronic state of the system can change during the reaction. Our work for this project has considered nonadiabaticity induced by spin-orbit effects that leads to intersystem crossing. The level of sophistication in theory that can be used for these problems varies considerably depending on the system being studied. In work before this project we studied the $S(^1D)$ + H_2/HD reaction with the Tully fewest switches approach, and with globally determined potential energy surfaces and couplings.[25] More recently we have collaborated with Keli Han at Dalian Institute of Chemical Physics to perform quantum dynamics calculations with these same surfaces.[26,27] This is excellent technology for simple systems, but its scaling with system size makes it impossible to use for larger systems.

An important step that we did more recently was the development of a simplified surface-hopping algorithm to describe ISC for the O + ethylene reaction.[28] In this approach, direct

dynamics is used to propagate trajectories on one surface, while simultaneously monitoring the energy of accessible surfaces with different spin. When crossings occur, a Landau-Zener approach is used to determine hopping probabilities. We used the B3LYP method to describe both singlet and triplet surfaces for this study, with spin-orbit parameters derived from complete-active-space self-consistent-field (CASSCF) calculations that were only done when the singlet and triplet states cross. This study demonstrated that intersystem crossing accounts for roughly half of O + C_2H_4 reaction at room temperature. Our results provided a nearly quantitative description of molecular beam results at low energy from Casavecchia's group. We also made predictions about the hyperthermal dynamics of this reaction which are different from the low energy results. Minton's group is planning to study these predictions with crossed-beams experiments.

II.2 Electron-impact-induced dissociation and photodissociation

New work was initiated during the project period concerned with electron impact induced dissociation of methane, and with related photodissociation processes. The electron impact work is based on the plane wave Born (PWB) expression for the electron-impact-excitation cross section, together with direct dynamics methods for characterizing the dissociation mechanism of the excited states. For the electron-impact-excitation cross section, we collaborated with Robert Buenker (Germany) to calculate generalized oscillator strengths that are need to determine PWB cross sections, and we were able to reproduce previous results for the excitation of H_2 which demonstrated that the scaled plane wave Born cross section is in quantitative agreement with experiment. We then applied this approach to methane, where unlike H_2 there are perhaps 100 electronic states to study, and there are issues with determining autoionization rates which factor into the impact/dissociation cross sections. Our initial results[29] were about half of the measured values at high energies, and there are important errors in the threshold region. This error is consistent with some of the earlier studies using the scaled plane wave Born method, so perhaps that is all that can be expected with this technology. However it is clear that more work is needed on this problem.

Better quality results were obtained in a study of the VUV photodissociation dynamics of methane.[30] In contrast to electron-impact-dissociation, VUV excitation only excites one or two excited states. The difficult task in this case was to study the dissociation dynamics, as several possible fragments can be produced, and both nonadibatic and adiabatic dynamics are possible. To do these studies we used the CASSCF direct dynamics combined with trajectory surface hopping based on the NEWTON-X/COLUMBUS code. We found that even though CASSCF is only capable of describing the excited state energies to without about 1 eV, the branching into product channels (CH_3+H, CH_2+H_2, CH + H + H_2) is essentially perfect.[30] In addition, the distribution of hydrogen atom translational energies is in quantitative agreement with experiment, and we were able to explain why a bimodal distribution has been obtained. These results show great promise for the use of NEWTON-X/COLUMBUS for describing other nonadiabatic processes, including electron-impact dissociation.

II.3 Atom/surface collision dynamics

Reactions of atoms or ions with liquid or solid surfaces is a major challenge for dynamics studies. A major accomplishment for this was project was the development of a method for doing this using direct dynamics in which the part of the system where bond-breaking takes place is described using electronic structure calculations, while the rest of the system is described

using empirical potentials. We initially applied this method to the collision of O or F atoms with the hydrocarbon liquid squalane (for which there are many experiments) and subsequently we studied ionic liquids (which is a nonconventional fuel of current interest). The O + squalane[31] studies provided detailed information about the spatial distribution of reactive sites and the correlation of reaction mechanism with the angular and translational distribution of the scattered products (OH, H, CH_3, CH_3O), giving a good mechanistic understanding of beam-surface experiments in the Minton lab.[32,33] We also identified products that were not detected in the experimental studies; providing stimulus for subsequent molecular beam measurements where they were seen.[34] Our F + squalane studies[35] have been used to interpret experiments done by David Nesbitt at thermal collision energies,[36-38] showing that there is a component of the HF product vibrational and rotational distributions which involves escape of HF from the surface with little relaxation. Our studies of hyperthermal atomic oxygen reacting with ionic liquids has involved a collaboration with Tim Minton, who has performed molecular beam studies involving ionic liquids with relatively high hydrocarbon content.[39] In these studies, OH is an important gaseous product just as with squalane as the liquid, however the ionic liquid is much denser, so OH production is more confined to regions of the surface where hydrocarbon chains are exposed. In a second study[40] we considered an ionic liquid with lower hydrocarbon content, and we found that very little OH is produced, but other products which involve abstraction and addition-elimination reactions are important. We also found examples of collision induced reaction between anion and cation, which is a process that would play an important role in hypergolic ionic liquids.

In addition to studies of hyperthermal atoms/ions interacting with liquids, we have also performed selected applications involving carbon-based solid surfaces. Our first work in this area[41] was concerned with characterization of oxidized graphene structures. This work has provided important predictions concerning the mechanisms for formation of oxidized graphite, including the steps needed to create holes in an undefected graphite surface,[41] and the mechanisms for formation of gaseous species including CO, OH, H_2O and CO_2. This work has also contributed to an understanding of the effect of holes and other defects on the mechanical properties of nanomaterials.[42-46] Recently[47] we have been involved in studies of the O + graphite collision system as part of a collaboration involving Tim Minton, who has performed experimental studies.[48,49] Here we focused on mechanisms that lead to the formation of CO or CO2, and we established the pathway whereby undefected graphene can become defected, which is the initial stage associated the formation of etch pits.

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